Chemical Structure of Poly (Vinyl Alcohol) - Styrene Graft Copolymer Prepared by Pre-Irradiation Technique (Special issue on Physical, Chemical and Biological Effects of Gamma Radiation, X)

AUTHOR(S):

Sakurada, Ichiro; Ikada, Yoshito; Horii, Fumitaka

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Ichiro SAKURADA, Yoshito IKADA and Fumitaka HORII*

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The chemical structure of poly(vinyl alcohol) (PVA)-styrene (St) graft copolymer prepared by pre-irradiation technique was studied by isolating the pure graft copolymer from the homoPSt and the ungrafted PVA. After complete benzoylation of the PVA backbone of the graft copolymer, fractionation was carried out by fractional precipitation method, and the chemical composition of each fraction was determined by ester exchange of the benzoyl groups in the graft copolymer. The grafted branches of fractions were separated from the backbone by cleaving 1, 2-glycol bonds in the PVA molecule, and osmotic pressure measurements were carried out for the fractionated graft copolymers and the separated branches after benzoylation of the PVA parts. By these measurements, it was possible to estimate the length of the backbone as well as of the branch. From the results it was concluded that this graft copolymer carried only one grafted branch, and that the backbone is formed from several mother PVA molecules which are crosslinked with each other. The molecular structure of this graft copolymer is quite similar to that of the PVA-MMA graft copolymer which was made clear previously. The amount of PVA participating in the grafting reaction was found to be only 9.6 %.

INTRODUCTION

The present work is a continuation of a series of studies aimed at the characterization of poly(vinyl alcohol) (PVA) graft copolymers prepared by various methods. In a previous paper[1] we have described the chemical structure of the PVA-methyl methacrylate (MMA) graft copolymer prepared by pre-irradiation technique, and elucidated that each graft copolymer consists of only one branch and several mother PVA molecules.

The present study was carried out to confirm whether the same result is obtained when some other monomer is grafted onto PVA with similar irradiation technique. The polymer studied here is PVA-styrene (St) graft copolymer.

EXPERIMENTAL

1. Graft Copolymerization

PVA-St graft copolymer was prepared in a similar way as for the PVA-MMA graft copolymer described in the previous paper[1]. The outline of the grafting procedure is as follows. PVA films were pre-irradiated in the presence of air at room temperature to a dose of 1.0×10^6 r and then immersed in a degassed

* 桜田 一郎, 筏 義人, 堀井 文敬 : Department of Polymer Chemistry, Kyoto University, Kyoto

methanol solution of monomer containing carbon tetrachloride (CCl_4), which was used as a chain transfer agent. The composition of the monomer mixture was as follows: St : CCl_4 = 1 : 0.03 (by mole), St : methanol = 40 : 60 (by vol.). 200 ml of monomer solution was used for 3.50 g PVA. The amount of CCl_4 to be added was determined on the basis of results obtained in an earlier work[2], where the effect of CCl_4 on the graft copolymerization of St onto PVA films was studied intensively, and the chain transfer constant of CCl_4 was found to be 8.0×10^{-3}. The PVA used is a fractionated one with a degree of polymerization (DP) of 1,280. The graft copolymerization was carried out for 120 hrs, rotating incessantly the sealed ampoule for the polymerization in a water bath kept at 50°C.

2. Extraction of Homopolymer

After removal of the homoPSt formed outside of the films, the homoPSt entrapped in the grafted films was extracted with boiling benzene, exchanging repeatedly the solvent for the freshly distilled one. When the homoPSt could not be extracted anymore, boiling water was used as a solvent for extraction of the ungrafted PVA. This alternate extraction was repeated till no more homoPSt and ungrafted PVA were extracted. The residue, which remained after the thorough alternate extraction, was regarded as the pure graft copolymer. It was confirmed from the infrared spectra that both extracted polymers contained no appreciable amount of graft copolymer.

3. Esterification

In order to fractionate the graft copolymer and estimate the molecular weight of the fractions, it is strongly required that the graft copolymer can be dissolved molecularly in a solvent. For the PVA-St graft copolymer, only hot dimethyl formamide (DMF) was found to be the solvent. However, PVA degrades in this solvent, although very gradually. Therefore, to make the graft copolymer soluble in ordinary solvents at room temperature, the hydroxyl groups in the PVA part of the isolated graft copolymer were benzoylated in a benzoic anhydride-pyridine (1 : 2) mixture at 100°C for 77 hrs. In the case of PVA-MMA graft copolymer, the hydroxyl groups were acetylated, because complete compatibility was obtained between the backbone polymer and the branch in benzene. In the present case the PVA was not acetylated, but benzoylated, since the compatibility of PSt with poly(vinyl benzoate) (PVBz) was much better than with poly(vinyl acetate) (PVAc). For instance, the critical polymer concentration for occurrence of phase-separation was 2.3 wt% for a PVAc-PSt (1 : 1) mixture in benzene at 30°C, which was broadened to 4.1 wt% for a PVBz-PSt (1 : 1) mixture. (DP's of PVAc, PSt and PVBz used for this phase-separation study were 1,280, 1,800 and 1,700, respectively). The ester exchange of benzoylated graft copolymers was effected in a benzene-methanol mixture with N/4 methanolic NaOH at 30°C for 4 hrs. The content of vinyl benzoate was calculated from hydrolysis of methyl benzoate which was formed as a result of the ester exchange of the benzoylated graft copolymer. The chemical composition estimated in this way was in good agreement with that calculated from elementary analysis. For example, the content of hydroxyl groups was found 45.9 mole% (ester exchange) and 45.6 mole% (ele-

mentary analysis). Thus, all of them in the graft copolymer can be regarded to be benzoylated.

4. Fractionation

The benzoylated graft copolymer was fractionated carefully by fractional precipitation method. Among many combinations of solvent-precipitant, tetrahydrofuran(THF)-*n*-propanol was chosen as an adequate combination for the fractionation, since this system gave the nearly same r-value ($=n$-propanol/THF) for precipitation of PSt and PVBz. The fractionation was carried out at 30°C by dropwise addition of *n*-propanol to 1 wt% THF solution of the graft copolymer.

5. Separation of Branch

After the PVBz part of the graft copolymer was again converted to PVA, the PSt branches of the graft copolymer were separated away from the PVA backbone by cleaving 1, 2-glycol bonds in PVA. The cleaving reaction was carried out with sodium periodate in 1 wt% DMF solution at 120°C for 5 hrs. Since a short PVA chain with DP of about 50~100 attached at the end of the separated branch might hinder the molecular dissolution of the branch polymer in such a solvent as benzene, the pendent short PVA chain was again benzoylated before the measurement of the molecular weight of the branch polymers.

6. Measurement of Chemical Composition and Molecular Weight

The chemical composition of each fraction of the graft copolymer was determined by ester exchange of the benzoylated branch part in the graft copolymer. The number-average molecular weights of the fractionated graft copolymers and the separated branches were determined by osmometry in benzene solution at 30°C. The osmometer used is "501 High-Speed Membrane osmometer" (Mechrolab Inc.) and the semipermeable membrane is gel cellophane. For comparison with the benzoylated graft copolymer, the osmometry was also carried out for the acetylated graft copolymer.

RESULTS AND DISCUSSION

1. Isolation of Graft Copolymer

As is well-known, fractional precipitation and selective extraction are most representative methods to isolate the graft copolymer from the homopolymer formed and the ungrafted substrate polymer. Recently, we have shown that the selective extraction is an effective method, although it takes plenty of time[1,2]. Also in the present study the graft copolymer was isolated by the selective alternate extraction with boiling benzene for the homoPSt and boiling water for the ungrafted PVA. The result of the alternate extraction is shown in Fig. 1, where it can be seen that the homoPSt and the ungrafted PVA are extracted successfully by means of the alternate extraction, as observed in the previous case of the grafting of MMA onto PVA. The percent grafting and the graft efficiency calculated after the complete extraction were found to be 12.5% and 8.2%, respectively, whereas the percent grafting and the graft efficiency were so high as 57.5% and 37.8%, respectively, when calculated on the basis of the data obtained

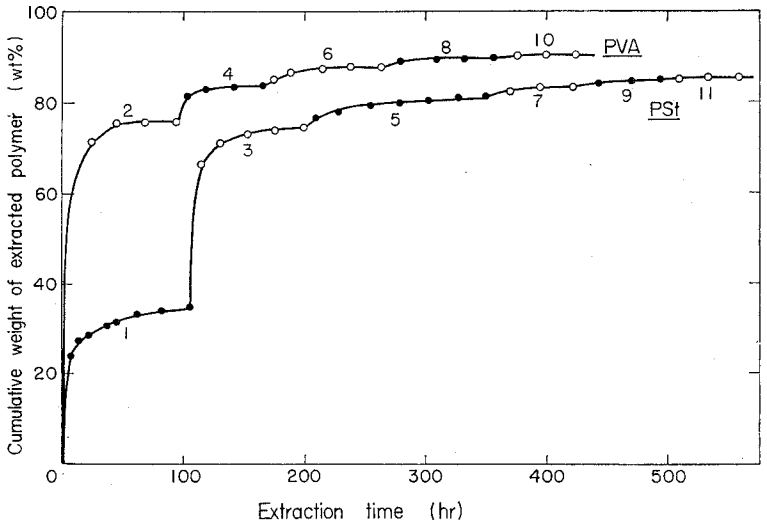

Fig. 1. Alternate extraction of the homoPSt and the ungrafted PVA.

after the conventional extraction. It is noteworthy that the fraction of PVA participating in the grafting reaction was only 9.6% of the starting PVA. The reason for this low value may be that the grafting occurred probably only in the vicinity of the surface of films owing to low permeability of the monomer into PVA films. This explanation is supported also by the fact that the grafted films became hollow like beanpod, as the extraction of the ungrafted PVA proceeded.

The viscosity-average DP's of the extracted homopolymers are plotted against the extraction time in Fig. 2. It can be seen that the homoPSt and the ungrafted PVA are extracted more readily when the DP of the polymer is lower. This tendency was also found in the case of graft copolymerization of MMA. One different feature of the present study from that of the PVA-MMA grafting system is that the homoPSt was formed only on the surface or in the interior of films, but none in the outer solution, while plenty of homoPMMA was formed in the

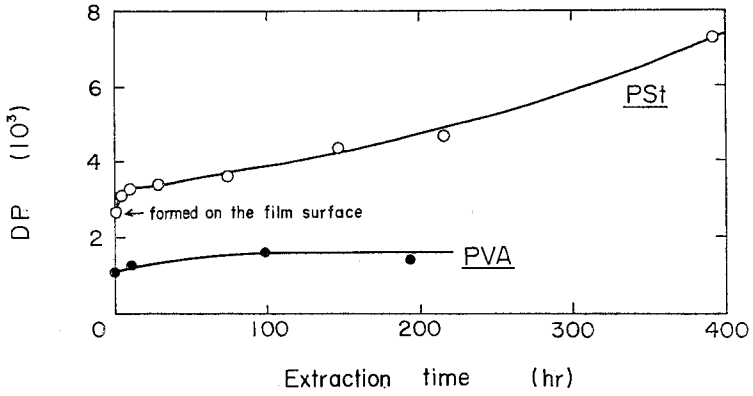

Fig. 2. DP of the extracted homoPSt and the ungrafted PVA.

outer solution at the grafting of MMA. This may be due to the difference of precipitation power of methanol to PMMA and PSt.

2. Fractionation of Benzoylated Graft Copolymer

A clear phase-separation was observed also in this case, similarly to the fractionation of the PVAc-MMA graft copolymer, although the compatibility of PVBz with PSt was not so excellent as that of PVAc with PMMA. The results of fractional precipitation are given in Figs. 3 and 4. As is obvious from Fig. 4, molecular weights of fractions vary remarkably over the wide range, while the variation of the chemical composition is not so significant. This means that the fractionation has taken place, depending mainly on the molecular weight,

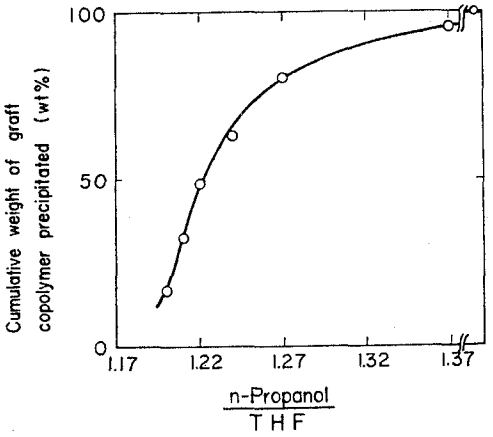

Fig. 3. Fractional precipitation curve of the PVBz-St graft copolymer.

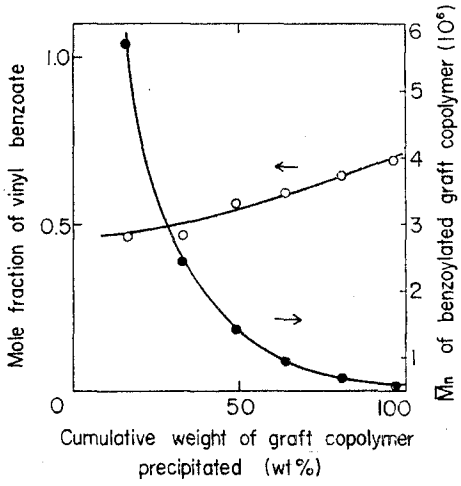

Fig. 4. Chemical composition and molecular weight, M_n, of the fractionated PVBz-St graft copolymers.

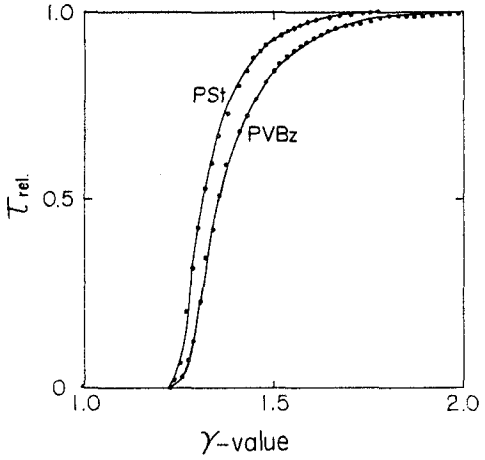

Fig. 5. Turbidimetric titrations for PVBz (DP=1,700) and PSt (DP=2,000) in 0.01 wt% THF solution at 30°C with *n*-propanol as a precipitant.

but not on the chemical composition. This finding accords with that observed for PVA-MMA graft copolymer. Fig. 4 demonstrates that the content of benzoyl group becomes gradually higher as the fractionation proceeds. This may be caused by stronger precipitation power of *n*-propanol to PSt than that to PVBz. It was confirmed, in fact, by a turbidity measurement of THF solutions of PVBz and PSt. As shown in Fig. 5, PSt precipitates more readily with addition of *n*-propanol than PVBz does.

3. Chemical Structure of Graft Copolymer

The observed number-average molecular weights, M_n, of benzoylated graft copolymers and of separated branches are summarized in Table 1. In order to ascertain whether the values of M_n of the graft copolymer are really correct, in other words, the graft copolymers were dissolved in benzene molecularly or not, M_n of the benzoylated graft copolymer was compared with that of acetylated graft copolymer, using an unfractionated graft copolymer. The result is given in Table 2, where it can be seen that DP of the benzoylated graft copolymer is somewhat higher than that of the acetylated, but the difference is not predominant. If the association of the copolymers could take place in benzene, it seems likely that the acetylated graft copolymer might associate more readily than the benzoylated, resulting in higher DP. The result given in Table 2 shows rather an opposite tendency. Thus the measured M_n's in Table 1 can be regarded to indicate valid values.

Table 1. Molecular weight and chemical composition of fractions.

Fraction number	M_n (10^5)		Chemical composition		
	Benzoylated graft copolymer	Separated branch	wt. fraction		mole fraction
			St	VBz	VBz
1	57.2	19.8	0.441	0.559	0.471
2	24.5	12.9	0.436	0.564	0.476
3	14.3	6.44	0.347	0.653	0.569
4	9.2	3.97	0.314	0.686	0.606
5	6.97	2.94	0.274	0.726	0.651
6	5.66	1.73	0.232	0.768	0.700

Table 2. Comparison of degrees of polymerization of differently esterified PVA-St graft copolymers (Sample: No. 2)

Esterification	Composition (St mole%)	M_n (10^5)	DP
Benzoylation	54.1	10.3	8,300
Acetylation	54.1	6.43	6,730

Although a considerable amount of CCl_4 was added to the polymerization system, M_n's of the graft copolymers are in most cases relatively high, ranging in the vicinity of the upper limit of the molecular weight measurable by ordinary osmometry. However, this uncertainty of absolute values may not influence so

seriously on the general discussion about the chemical structure, since it is sufficient only to compare M_n with each other in order to obtain information of the number of branch. Table 3 lists the numbers of the branch and the mother PVA molecules contained in one graft copolymer molecule. They were calculated by the method described in the previous paper[1]. As can be seen from Table 3, the numbers of the branch are slightly different from unity, but when experimental errors are taken into consideration, they can be regarded as nearly unity. Thus it may be concluded that only one branch is grafted on each backbone. This conclusion is quite the same as that drawn for the PVA-MMA graft copolymer prepared by pre-irradiation technique.

Table 3. Number of branch and mother PVA in one fractionated graft copolymer.

Fraction number	Weight fraction (%)	Number of branches	Number of mother PVA molecules
1	16.2	1.28	16.9
2	16.4	0.84	7.16
3	15.9	0.78	4.92
4	14.6	0.73	3.32
5	17.8	0.64	2.63
6	15.2	0.75	2.27

It is very seldom that the length of the backbone part in graft copolymers has been estimated[3~5]. In most cases, this is assumed to be equal to the mother substrate molecule. According to the result given in Table 3, the backbone of the graft copolymer consists of not one, but of several mother PVA molecules. This finding is thoroughly identical to that obtained in the previous study of the PVA-MMA graft copolymer, and it may be explained similarly by formation of crosslinking among the mother PVA molecules through CCl_4. In fact it was found that PVA films became partially insoluble when heated in CCl_4-methanol mixture[6].

Fig. 6 shows the DP distribution of the graft copolymer and the branch polymer, which was calculated on the basis of the results given in Tables 1 and 3. The results of Fig. 6 show that the DP distribution of the graft copolymer is remarkably broad and has only one peak. This result is, however, apparently different from that obtained by Wellons, Schindler, and Stannett[7], who found that the branch polymer of the cellulose acetate-St graft copolymers prepared by the pre-irradiation technique had a two-peak distribution. To make clear this difference, more available information will be necessary. From the DP distribution curve of the graft copolymer and the chemical composition of each fraction, the average number of mother PVA molecules in the whole graft copolymer was calculated to be 3.3. It is interesting to point out here that, as obvious from the comparison of results in Fig. 6 with those in Fig. 2, the lengths of branch can be taken to be approximately equal to those of homopolymers formed in the interior of the films. This equality was found also in the case of PVA-MMA graft copolymer.

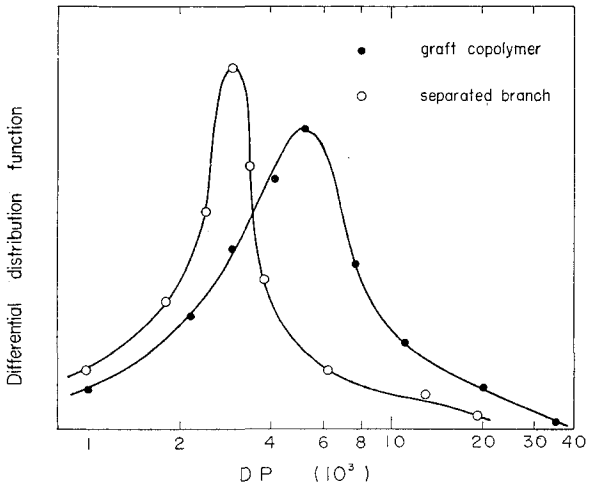

Fig. 6. DP distribution curves of the PVA-St graft copolymer and the separated branch.

One of the most basic problems in the grafting field may be to confirm whether the grafting reaction takes place really or not. As far as we know, no conclusive evidence for the existence of true graft copolymer has so far been provided, although a few methods[8~10] for this purpose have been proposed and applied actually for several cases. For instance, the density gradient centrifugation developed by Hermans and Ende[11] is an elegant method to check if a given sample is free from the other polymers, but it cannot distinguish whether a copolymer is the graft- or block-type. In our works, no direct attempt was tried to prove the existence of covalent linkage between the PVA and the branch. However, from the following reasons it seems highly plausible that the PVA and the branch are linked covalently. (1) The extraction of both the homopolymer and the ungrafted substrate was carried out to completion, and the residue was soluble only in DMF, which is the common solvent for PSt and PVA. (2) The calculated molecular weights of grafted branches were in good agreement with the observed values of branches separated chemically from the substrate molecules. (3) When unirradiated PVA films were immersed in the monomer solution and heated at 50°C in the same manner as the grafting reaction, no or only slight increase of the films was observed. (4) The behavior of phase-separation of this polymer in solutions was distinctly different from that of the mechanical mixture of the homopolymer and the substrate polymer. This result will be published in a future paper. The study aimed to obtain a direct evidence of covalent linkage between the branch and the backbone is now being carried out.

REFERENCES

(1) I. Sakurada, Y. Ikada, and Y. Uesaki, *Bull. Inst. Chem. Res., Kyoto Univ.*, 47, 49 (1969).

(2) I. Sakurada, Y. Ikada, T. Yamaoka, and F. Horii, *Bull. Inst. Chem. Res., Kyoto Univ.*, 46, 13 (1968).

(3) I. Mita, *J. Chim. Phys.*, **39**, 530 (1962).
(4) J. Jozefowicz, *Int. Sym. Macromol. Chem.*, p. 579 (Prague 1965).
(5) J. D. Wellons and V. Stannett, *J. Polymer Sci.*, **A3**, 847 (1965).
(6) unpublished work.
(7) J. D. Wellons, A. Schindler, and V. Stannett, *Polymer*, **5**, 499 (1964).
(8) C. P. J. Glaudemans and E. Passaglia, *J. Polymer Sci.*, **C1**, 189 (1963).
(9) H. Yasuda, J. A. Wray, and V. Stannett, *J. Polymer Sci.*, **C2**, 287 (1963).
(10) H. A. Ende and V. Stannett, *J. Polymer Sci.*, **A2**, 4047 (1964).
(11) J. J. Hermans and H. A. Ende, *J. Polymer Sci.*, **C4**, 519 (1963).